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Health and Safety

AEC RESEARCH AND DEVELOPMENT REPORT



# CHARACTERIZATION OF Y-12 URANIUM PROCESS MATERIALS CORRELATED WITH IN VIVO EXPERIENCE (U)

L. M. Steckel
C. M. West

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

*operated for the* ATOMIC ENERGY COMMISSION *under* U. S. GOVERNMENT Contract W-7405 eng 26

UNION CARBIDE

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Health and Safety
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Oak Ridge, Tennessee

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## ABSTRACT

Twenty-two process materials from the Y-12 enriched uranium area were selected as suspect exposure materials to five employees showing internal chest burdens with long biological half lives. As a means of establishing which of these were the most likely exposure materials, measures were made of their solubility in a simulated lung fluid; each was characterized as to particle size, uranium composition, and other contaminants. Similar analyses were made on oxides prepared at known temperatures to further study the insolubility parameters.

The studies indicated that three process combustion ashes, containing uranium octoxide ($U_3O_8$), were the most likely exposure materials. These materials apparently differed from those used in previous animal studies in thermal history, particle size, and level of contamination. In view of these differences and the paucity of such animal data, it was recommended that animal experiments be conducted using these three ashes

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## SUMMARY

In vivo monitoring results on five Y-12 Plant employees have shown uranium chest burdens with long biological half lives of from 380 to 1470 days. Because of the unusual nature of these cases, it was considered important to define the responsible exposure material(s).

Detailed work and exposure histories of the five employees were used to select twenty-two uranium process materials to which these employees were most likely to have been exposed.

These selected materials were subjected to extensive chemical and physical tests to determine which material had the characteristics that would most likely result in high biological insolubility and a long retention period in the lung. The tests consisted of a check for solubility in a simulated lung fluid and characterization as to uranium content, chemical composition, particle size, and contamination.

Results of the tests showed that some of the compounds selected contained concentrations of uranium too small to be likely exposure materials; others were too soluble in the simulated body fluids to warrant serious consideration as the exposure material(s). Twelve of the materials appeared to have the characteristics necessary to make them possible exposure materials. Ten of the 12 materials were found to contain uranium octoxide ($U_3O_8$), making it the most likely exposure compound.

These oxide-containing materials differed in solubility by factors of up to 30. To better define the reason for this variability and to further explore the insolubility parameters, similar studies were made on laboratory oxides prepared with known temperatures of formation.

These studies proved that the solubility of such oxides could be related to the parameters of chemical composition and/or particle size. Oxygen-to-uranium ratios decreased, while particle size increased with increasing temperature of formation. This study also revealed that the technique used for compound identification in the process material study would not detect the more soluble uranium trioxide component. This fact possibly accounted for some of the variability in process samples previously considered to contain only the octoxide. The information obtained from the various tests led to the selection of three process combustion ashes containing uranium octoxide as the most likely exposure materials.

Previous animal experimentation using oxides of uranium indicated a lung or chest half life of approximately 120 days, thus introducing an apparent contradiction. However, further inspection of the data indicated that the selected process exposure materials have a larger particle size, higher heats in their thermal histories, and greater concentrations of contaminants than did the oxides used in animal studies. In view of these differences in animal experiment and Y-12 process oxides and the

paucity of the animal data available, it is concluded that animal studies are needed using the three most likely exposure materials. Such a study should ascertain whether or not these materials have a long enough half life, in vivo, to be the exposure material in the Y-12 cases.

# INTRODUCTION

A relatively large part of the Y-12 Plant population has been involved in processing uranium during more than twenty years of plant operation. During the last five years, some 2500 employees have been monitored routinely by in vivo gamma spectrometry(1) as a part of the uranium internal-exposure evaluation program.

During the period, in vivo monitoring results for five employees indicated chest burdens with biological half lives of from 380 to 1470 days.(2) The nominal biological half life expected for uranium in the lung is 120 days;(3) and, except for the five cases, Y-12's experience has confirmed the validity of such a half-life value. Efforts have been initiated to determine the reasons for these unexpectedly long retention periods. Comprehensive physical examinations of the people involved revealed no physiological causes for these unusual patterns. Complete work and exposure histories, compiled for the periods when it was suspected the exposures occurred, failed to give definitive information on the identity of the specific exposure materials.

In a further effort to define the exposure materials, work histories were used to select uranium process materials to which these employees were most likely to have been exposed. Extensive physical and chemical tests were made to characterize these materials. This characterization was designed to determine which material had properties that would most likely result in long biological retention in the lung. Other process materials were included for comparison, and additional studies were made on laboratory-prepared materials. This report describes the tests made, presents the results obtained, and comments on the in vivo implications of such information.

# CHARACTERIZATION STUDIES

## PROCESS MATERIALS

### Collection and Analysis

Samples were collected from areas involved with processing uranium enriched to approximately 93% in U-235. Selection was made on the basis of past experience and in relation to the case histories of inhalation exposures. All samples (which weighed several hundred grams each) were thoroughly blended to reduce segregation, then a 25-gram portion of the sample was removed for study. The bulk of all samples was stored.

Table 1 lists all of the process samples that were studied along with the general analyses that were made on the samples to aid in their characterization. The uranium content was determined by standard spectrophotometric or potentiometric methods, depending on the uranium concentration. The various other cations were determined by a semiquantitative spectrographic technique. (The tabulation includes only those cations present in amounts equal to or greater than 2.5 percent.) A standard powder-pattern technique was used in the X-ray diffraction studies.(4, 5) X-ray diffraction studies on the two process uranium trioxide samples (Specimens 2 and 3) revealed only a weak pattern for the compound $UO_3 \cdot 0.8\ H_2O$, thus indicating an essentially amorphous matrix.

### Solubility Studies

Description - Solubility studies were designed on the premise that the substances were difficult to dissolve. An equilibrium saturated solution condition was never anticipated. To this extent, the term "solubility" is used as a matter of convenience, and is acknowledged to be technically incorrect.

Two basic approaches were utilized in achieving a measure of the solubility of these materials in a snythetic lung fluid. (In both instances, the amount of uranium dissolved was presumed limited by the time interval of contact.) One approach involved a variable contact interval, referred to as the "sixteen-week study", while the second approach, known as the "recycle study", involved repeated exposure of the same solids to fresh solutions on a fixed-time-interval basis.

The twenty-two uranium process materials selected for characterization in this study were tested for solubility in a synthetic liquid which simulated a lung or interstitial fluid medium. This synthesized medium permitted solubility studies to be carried out for relatively long intervals without the bacteriological action which could occur in natural body fluids.

Table 1

PROCESS SAMPLE DESCRIPTIONS

| Sample Number | Description | Value (gm U/gm) | Other Cations Present (≥ 2.5%) | Compounds Identified by X-Ray Diffraction | | |
|---|---|---|---|---|---|---|
| | | | | Major | Intermediate | Minor |
| 1 | $UF_4$ - Type A | 0.7558 | ND[3] | NA[4] | - | - |
| 2 | $UO_3$ - Type A | 0.8180 | ND | ND | - | $UO_3 \cdot 0.8\ H_2O$ |
| 3 | Reclaimed Sand[1] | 0.001819 | 7.5% Ca, > 20% Mg | NA | - | - |
| 4 | High U Ash | 0.4659 | 2.5% Al, 5% Fe, 12% Si, 5% Zn, ~6% Zr | $U_3O_8$ | ND | $Fe_2O_3$, $Zn(OH)_2$ (?), $Al_2SiO_5$, $ZrO_2$ |
| 5 | Carbon Ash - I | 0.4425 | 15% Al, 7% Ba, 15% Fe, 10% Si, 4% Zr | $U_3O_8$ | ND | $UO_2$ (?) |
| 6 | Carbon Ash - II | 0.3841 | 15% Fe, 8% Si, 4% Zr | $U_3O_8$ | ND | Possibly: $Fe_2O_3$, $CaCO_3$, $BaSi_2O_5$, $ZrO_2$ |
| 7 | $UO_3$ - Type B | 0.8220 | ND | ND | - | $UO_3 \cdot 0.8\ H_2O$ |
| 8 | $UF_4$ - Type B | 0.7554 | ND | NA | - | - |
| 9 | Caustic Fusion Residue[2] | 0.001687 | 4.5% Al, 3% Cr, 2.5% Fe, 2.5% Na, > 20% Si, 4% Zr | $SiO_2$ | ND | $ZrO_2$ (?) |
| 10 | Column Leacher Residue | 0.01639 | 12% Al, 2.5% Ba, 2.5% Cr, 15% Fe, > 25% Si, 2.5% Zn, ~6% Zr | $ZrSiO_4$ | $ZrO_2$, $SiO_2$ | $Fe_2O_3$ |
| 11 | Firebrick | 0.00459 | > 20% Al, > 30% Si | $Al_2O_3$, $Al_6Si_2O_{13}$ | $SiO_2$ | Alpha - $Fe^o$ (?) |
| 12 | Salvage - I | 0.005193 | > 20% Ca, > 20% Mg | $CaF_2$ | MgO | $Ca(OH)_2$, LiF (?) |
| 13 | High U Oxide - I | 0.8306 | ND | $U_3O_8$ | ND | ND |
| 14 | High U Oxide - II | 0.8269 | ND | $U_3O_8$ | ND | ND |
| 15 | Filter Bag Ash | 0.2809 | 5% Mg, 10% Si, ~8% Zr | $ZrSiO_4$ | $U_3O_8$, $ZrO_2$ | $Fe_2O_3$, $SiO_2$ (?) |
| 16 | Paper Ash - I | 0.3321 | 5% Fe, ~18% Si, 5% Zr | $U_3O_8$ | ND | Possibly: $Fe_2O_3$, $ZrSiO_4$, $ZrO_2$ |
| 17 | Unleached Ash | 0.08735 | 11% Al, 10% Ca, 5% Cr, 17% Fe, 3% Mg, 3.5% Na, 2.5% P, 7% Pb, 12% Si, ~15% Zn | $Al2SiO5$, $Fe2O3$, ($Na_2$, $K_2$, Ca, Pb) $U_2O_7 \cdot nH_2O$ | ND | Alpha - $Fe^o$, $Zn^o$, $U_3O_8$ |
| 18 | Carbon Ash - III | 0.7580 | 5% Fe | $U_3O_8$ | ND | $UO_2$ (?) |
| 19 | Paper Ash - II | 0.1587 | 10% Al, 9% Ca, 10% Cr, 15% Fe, 12% Si, 10% Zn | $U_3O_8$ | $NaAl(SiO_3)_2$ | $Fe_2O_3$, $CaCO_3$ (?), $SiCl_4$ (?) |
| 20 | Salvage - II | 0.1688 | 13% Al, 4.5% Ba, 5% Cr, 15% Fe, 5% P, 14% Si, 3% Zr | $ZrSiO_4$ | $Fe_2O_3$, $ZrO_2$ | $SiO_2$ AlN (?) |
| 21 | High-Fired $UO_2$ | 0.8768 | ND | NA | - | - |
| 22 | Burned Uranium Chips | 0.8456 | ND | NA | - | - |

(1) Sample appears inhomogeneous.
(2) Results on dried sample. To convert to as-received material, multiply by 0.418.
(3) ND indicates none detected.
(4) NA indicates no analysis.

The synthetic lung fluid was prepared using the composition described by Gamble.[6] Table 2 gives the ionic concentration of the synthetic lung fluid that was used. Acetate was substituted for all organic-acid anions plus protein. The 0.4 percent protein listed by Gamble was omitted to prevent possible bacterial action.

Table 2

IONIC CONCENTRATION OF SYNTHETIC LUNG FLUID

| | Concentration (mgs/l) |
|---|---|
| Cations | |
| Magnesium | 25.3 |
| Calcium | 69.5 |
| Potassium | 163.0 |
| Sodium | 3384.1 |
| Anions | |
| Sulfate | 53.3 |
| Monohydrogen Phosphate | 99.8 |
| Chloride | 4088.5 |
| Bicarbonate | 1867.2 |
| Organic Acids (as acetate) | 462.3 |

Sixteen-Week Study - Each 25-gram portion of the process material sample was again blended. Fifty milligrams of each sample and 50 milliliters of the synthetic lung fluid were placed in closed polystyrene containers. These samples were maintained in a shaking incubator at body temperature (37° C) for contact periods of 1, 2, 4, 8, or 16 weeks. The samples were then removed from the incubator and allowed to stand overnight at room temperature (24° C) before sampling for soluble uranium.

A 20-milliliter sample of the synthetic lung fluid was removed through a 0.45-micron filter (Appendix A), acidified with nitric acid, and diluted to 25 milliliters. The uranium content of the sample was determined in duplicate by fluorometric analysis. If an upper limit of 25 µgs/ml was exceeded, the sample was analyzed spectrophotometrically using a dibenzoylmethane procedure.

A majority of the samples were analyzed fluorometrically by pipetting a 100-lambda portion of the sample directly onto a sodium fluoride-lithium fluoride (98:2) flux in a platinum dish which, after drying, was fused into a button. The result was then read on a fluorometer. Table 3 summarizes the results of the sixteen-week study.

Recycle Study - In another phase of the solubility study, a 50-milligram sample was "exposed" to 50 milliliters of synthetic lung fluid for one week in the incubator and

Table 3

SOLUBILITY OF PROCESS SAMPLES AT VARIOUS CONTACT INTERVALS

| Sample Number | Description | Major Uranium Compound Present | Total Uranium Present (µgs) | Time Interval and Total Uranium Dissolved (%) | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 1 Week | 2 Weeks | 4 Weeks | 8 Weeks | 16 Weeks |
| 1 | $UF_4$ - Type A | $UF_4$ | 37,800 | 3.3 | 5.0 | 16.0 | 39.1 | 59.4 |
| 2 | $UO_3$ - Type A | $UO_3$ | 40,900 | 56.7 | 92.6 | 98.5 | 105.0 | - |
| 3 | Reclaimed Sand(1) | - | 91 | 2.0 | 0.1 | 0.1 | 1.8 | 2.4 |
| 4 | High U Ash | $U_3O_8$ | 23,300 | 0.6 | 0.6 | 0.6 | 0.6 | 2.4 |
| 5 | Carbon Ash - I | $U_3O_8$ | 22,100 | 0.9 | 0.8 | 0.9 | 1.2 | 1.3 |
| 6 | Carbon Ash - II | $U_3O_8$ | 19,200 | 0.8 | 0.6 | 0.7 | 2.0 | 1.6 |
| 7 | $UO_3$ - Type B | $UO_3$ | 41,100 | 59.0 | 79.5 | 97.6 | 106.0 | - |
| 8 | $UF_4$ - Type B | $UF_4$ | 37,700 | 3.2 | 6.3 | 8.0 | 40.3 | 69.8 |
| 9 | Caustic Fusion Residue(2) | - | 35 | ~ 60.0 | ~ 31.0 | ~ 29.0 | ~ 34.0 | ~ 45.0 |
| 10 | Column Leacher Residue | - | 820 | ~ 16.0 | ~ 18.0 | ~ 16.0 | ~ 20.0 | ~ 22.0 |
| 11 | Firebrick | - | 230 | 0.8 | 0.9 | 3.3 | 0.6 | 1.6 |
| 12 | Salvage - I | - | 260 | 5.8 | 4.8 | 6.0 | 7.7 | 13.0 |
| 13 | High U Oxide - I | $U_3O_8$ | 41,500 | 1.5 | 1.2 | 1.5 | 2.4 | 5.1 |
| 14 | High U Oxide - II | $U_3O_8$ | 41,300 | 1.5 | 1.0 | 1.1 | 3.0 | 3.5 |
| 15 | Filter Bag Ash | $U_3O_8$ | 14,050 | 0.8 | 0.7 | 0.8 | 1.0 | 1.4 |
| 16 | Paper Ash - I | $U_3O_8$ | 16,600 | 2.2 | 1.9 | 2.2 | 3.6 | 7.0 |
| 17 | Unleached Ash | (3) | 4,370 | ~ 13.0 | ~ 12.0 | ~ 13.0 | ~ 12.0 | ~ 16.0 |
| 18 | Carbon Ash - III | $U_3O_8$ | 37,900 | 0.3 | 0.2 | 0.2 | 0.4 | 0.6 |
| 19 | Paper Ash - II | $U_3O_8$ | 7,940 | 1.9 | 2.8 | ~ 11.0 | 3.4 | ~ 12.0 |
| 20 | Salvage - II | - | 8,440 | ~ 35.0 | ~ 34.0 | ~ 35.0 | ~ 32.0 | ~ 41.0 |
| 21 | High-Fired $UO_2$ | $UO_2$ | 43,800 | 0.3 | 0.2 | 0.2 | 0.2 | - |
| 22 | Burned Uranium Chips | $U_3O_8$ | 42,300 | 0.2 | 0.2 | 0.2 | 0.3 | - |
| 9(4) | Caustic Fusion Residue | - | 350 | ~ 43.0 | ~ 33.0 | ~ 35.0 | ~ 32.0 | ~ 41.0 |

(1) Sample appears inhomogeneous.
(2) Results on dried sample. To convert to as-received material, multiply by 0.418.
(3) Mostly a diuranate with some uranium octoxide.
(4) Solubility studies were made with 500 milligrams of sample because of the low uranium content of the sample.

a 20-milliliter sample removed for uranium analysis. Next, the excess synthetic lung fluid was filtered off through a 0.45-micron membrane filter and 50 milliliters of the new synthetic lung fluid added for another week of contact time with the sample. In this study, each sample was allowed to go through ten weekly cycles or was discontinued when the uranium solubility results were < 0.1 percent for three or more cycles. The results of this study showed general agreement with the sixteen-week study. A tabulation of the results of this solubility study is presented in Table 4.

Control Program - A control program involving solutions containing uranium at known concentration levels was maintained coincident with the solubility studies to assure the validity of the measurements. Details of the control program are presented in Appendix B. A related study of the adsorption of uranium on the walls of the polystyrene container is also contained in Appendix B.

## Particle Size Studies

For further characterization, the process samples were sieved and the less than 100-mesh fraction (< 150 μ) was subjected to further physical analyses. The surface area was determined by the BET (Brunauer-Emmett-Teller) method[7] which depends upon the adsorption of a monomolecular layer of nitrogen at a low temperature on the surface of the particle, thus producing a pressure difference that is proportional to the surface area of the particle. A helium gas displacement method was applied for the density measurement.[8] The average particle size ($\bar{X}$) of the process samples was calculated, as summarized in Table 5.

The average crystallite size was determined from the broadening effect of X-ray diffraction lines.[4] The crystallite-size determination was made on those samples in which the octoxide was the major compound, as shown by X-ray diffraction, and on the dioxide sample (Sample 21). The crystallite-size results are also included in Table 5.

## Discussion of the Results

Interpretation of the results from the solubility studies was made in the light of the ± 12 - 20% relative limit of error (0.95) obtained from a statistical evaluation of the control data (Appendix B).

There is a wide variation in solubilities exhibited by the process specimens (Table 3). It was felt that this variability might be attributable to the thermal histories of the samples. An effort was made to define the thermal histories of the process samples, but such information was found to be very sparse.

Solubility studies were made on the as-received basis. The physical analyses were carried out on the < 150 μ fraction, and the results do not necessarily correlate either with the as-received sample or the actual uranium-bearing particulates.

Table 4

SOLUBILITY OF PROCESS SAMPLES AFTER ONE-WEEK RECYCLES

| Sample Number | Description | Major Uranium Compound Present | Uranium Dissolved per Recharging (%) | | | | | | | | | | Total Uranium Dissolved (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | |
| 1 | $UF_4$ - Type A | $UF_4$ | 3.3 | 3.6 | 1.5 | 2.1 | 0.9 | 0.7 | 2.0 | 2.3 | 7.9 | 4.1 | 28.4 |
| 2 | $UO_3$ - Type A | $UO_3$ | 56.7 | (1) | - | - | - | - | - | - | - | - | 56.7 |
| 3 | Reclaimed Sand(2) | - | 2.0 | 2.3 | 0.1 | <0.1 | <0.1 | <0.1 | - | - | - | - | 4.4 |
| 4 | High U Ash | $U_3O_8$ | 0.6 | 0.3 | <0.1 | <0.1 | <0.1 | <0.1 | - | - | - | - | 0.9 |
| 5 | Carbon Ash - I | $U_3O_8$ | 0.9 | <0.1 | <0.1 | <0.1 | <0.1 | - | - | - | - | - | 0.9 |
| 6 | Carbon Ash - II | $U_3O_8$ | 0.8 | <0.1 | <0.1 | <0.1 | <0.1 | - | - | - | - | - | 0.8 |
| 7 | $UO_3$ - Type B | $UO_3$ | 59.0 | (1) | - | - | - | - | - | - | - | - | 59.0 |
| 8 | $UF_4$ - Type B | $UF_4$ | 3.2 | 1.7 | 2.0 | 2.1 | 1.1 | 1.2 | 1.4 | 1.2 | 2.2 | 1.6 | 17.7 |
| 9 | Caustic Fusion Residue(3) | - | 60.0 | 2.6 | 0.3 | 0.3 | <0.1 | <0.1 | <0.1 | - | - | - | 63.2 |
| 10 | Column Leacher Residue | - | 16.0 | 1.0 | 0.4 | 0.3 | 0.5 | 1.7 | 1.7 | 2.0 | 4.7 | 1.1 | 29.4 |
| 11 | Firebrick | - | 0.8 | <0.1 | <0.1 | <0.1 | <0.1 | - | - | - | - | - | 0.8 |
| 12 | Salvage - I | - | 5.8 | 0.2 | 0.1 | 1.0 | 1.4 | 1.5 | 0.3 | 0.4 | 0.3 | 0.2 | 11.2 |
| 13 | High U Oxide - I | $U_3O_8$ | 1.5 | 0.2 | 0.1 | 0.1 | <0.1 | <0.1 | <0.1 | - | - | - | 1.9 |
| 14 | High U Oxide - II | $U_3O_8$ | 1.5 | 0.2 | 0.1 | 0.2 | <0.1 | <0.1 | <0.1 | 0.1 | 1.0 | 2.0 | 5.1 |
| 15 | Filter Bag Ash | $U_3O_8$ | 0.8 | <0.1 | <0.1 | <0.1 | <0.1 | - | - | - | - | - | 0.8 |
| 16 | Paper Ash - I | $U_3O_8$ | 2.2 | 0.3 | 0.1 | <0.1 | <0.1 | <0.1 | - | - | - | - | 2.6 |
| 17 | Unleached Ash | (4) | 13.0 | 1.1 | 0.1 | 0.1 | <0.1 | <0.1 | <0.1 | - | - | - | 14.3 |
| 18 | Carbon Ash - III | $U_3O_8$ | 0.3 | <0.1 | <0.1 | <0.1 | <0.1 | - | - | - | - | - | 0.3 |
| 19 | Paper Ash - II | $U_3O_8$ | 1.9 | 0.2 | <0.1 | <0.1 | <0.1 | <0.1 | - | - | - | - | 2.1 |
| 20 | Salvage - II | - | 35.0 | 2.5 | 0.5 | 0.4 | 0.1 | 0.1 | 0.6 | 1.4 | 1.5 | 2.0 | 44.1 |
| 21 | High-Fired $UO_2$ | $UO_2$ | 0.3 | <0.1 | <0.1 | <0.1 | <0.1 | - | - | - | - | - | 0.3 |
| 22 | Burned Uranium Chips | $U_3O_8$ | 0.2 | <0.1 | <0.1 | <0.1 | <0.1 | - | - | - | - | - | 0.2 |
| 9(5) | Caustic Fusion Residue | - | 43.0 | 4.0 | 0.5 | 0.2 | <0.1 | <0.1 | <0.1 | - | - | - | 47.7 |

(1) Discontinued because it was very soluble.
(2) Sample appears inhomogeneous.
(3) Results on dried sample. To convert to as-received material, multiply by 0.418.
(4) Mostly a diuranate with some uranium octoxide.
(5) Solubility studies made with 500 milligrams of sample because of the low uranium content of the sample.

Table 5

SURFACE AREA, DENSITY, PARTICLE SIZE, AND CRYSTALLITE SIZE OF THE LESS THAN 100-MESH FRACTION OF THE PROCESS SAMPLES

| Sample Number | Description | Percent < 100 Mesh(1) | Surface Area ($M^2$/gm) | Helium Density (gms/cc) | Average Particle Size (μ) | Average Crystallite Size (μ) |
|---|---|---|---|---|---|---|
| 1 | $UF_6$ - Type A | 25.7 | NA(2) | NA | NA | - |
| 2 | $UO_3$ - Type A | 16.5 | NA | NA | NA | - |
| 3 | Reclaimed Sand(3) | 0.2 | NA | NA | NA | - |
| 4 | High U Ash | 89.6 | 1.41 | 4.94 | 0.86 | 0.08 |
| 5 | Carbon Ash - I | 29.1 | 1.53 | 5.36 | 0.73 | - |
| 6 | Carbon Ash - II | 46.0 | 1.26 | 5.34 | 0.89 | 0.07 |
| 7 | $UO_3$ - Type B | 8.8 | NA | NA | NA | - |
| 8 | $UF_4$ - Type B | 31.1 | NA | NA | NA | - |
| 9 | Caustic Fusion Residue(4) | 73.1 | 4.77 | 2.46 | 0.51 | - |
| 10 | Column Leacher Residue | 83.5 | 10.62 | 3.20 | 0.18 | - |
| 11 | Firebrick | 62.3 | 0.56 | 3.20 | 3.4 | - |
| 12 | Salvage - I | 67.3 | 0.77 | 3.08 | 2.5 | - |
| 13 | High U Oxide - I | 79.7 | 1.12 | 7.58 | 0.71 | 0.18 |
| 14 | High U Oxide - II | 83.5 | 1.13 | 7.70 | 0.69 | 0.10 |
| 15 | Filter Bag Ash | 89.8 | 0.76 | 5.07 | 1.6 | - |
| 16 | Paper Ash - I | 74.9 | 6.22 | 4.72 | 0.20 | 0.06 |
| 17 | Unleached Ash | 80.3 | 3.88 | 3.43 | 0.45 | - |
| 18 | Carbon Ash - III | 82.4 | 0.73 | 7.67 | 1.1 | 0.12 |
| 19 | Paper Ash - II | 56.3 | 7.59 | 2.90 | 0.27 | 0.18+ |
| 20 | Salvage - II | 45.6 | 15.06 | 3.26 | 0.12 | - |
| 21 | High-Fired $UO_2$ | 99.8 | 0.59 | 10.3 | 0.99 | 0.16 |
| 22 | Burned Uranium Chips | 75.0 | 0.21 | 8.22 | 3.5 | 0.18+ |

(1) < 150 μ.
(2) NA indicates no analysis.
(3) Sample appears inhomogeneous.
(4) Results on dried sample. To convert to as-received material, multiply by 0.418.

While the methods used in obtaining the solubility data provided certain possibilities for error, there was no evidence in the results that any errors had been encountered. Laminar flow around the membrane filter would have produced erratic and high results; low results through adsorption of uranium ions on container walls was proved to be of no consequence by the container-adsorption study (Appendix B). There was a positive bias introduced due to the evaporation of the synthetic lung fluid. However, this loss of 1.5 - 2% of the fluid volume per week should have little effect on the relative solubilities of the difficultly soluble materials. The evaporation factor, however, largely explains the high summation values obtained for some of the soluble materials.

Examination of the results obtained from the variable-contact internal study in the light of achievable precisions of the measurement methods reveals only two measurements of serious doubt (at 4 weeks, Specimens 11 and 19, Table 3) out of a total of 111 entries. A similar examination of Table 4 indicates that all entries were acceptable with the exception of a few of the 7 - 10 week entries of the more soluble materials.

## LABORATORY-PRODUCED OXIDES

### Analytical Work

At the completion of the characterization study on the 22 uranium process samples, one of the major unanswered questions was the reason for the wide variation in solubilities. One of the possible contributors to this variability, the essentially undefined thermal history of the process samples, led to a "second phase" experiment. Evaluation of this parameter required the preparation of uranium oxides at various ignition temperatures under controlled laboratory conditions. Starting material for this study was uranium peroxide ($UO_4 \cdot 2H_2O$) which was ignited in an argon atmosphere at temperatures from 300 to 1300° C. These oxides, prepared by thermal reduction, were then characterized by essentially the same physical, chemical, and solubility tests that were used for the production samples. Details of the preparation of these oxides have been included in Appendix C.

Those oxides having known thermal histories were subjected to various physical and chemical analyses, namely: (1) X-ray diffraction;[4, 5] (2) surface area;[7] (3) density (helium);[8] (4) crystallite size;[4] (5) uranium(IV), uranium(VI), and total uranium; and (6) Karl Fischer water determination.[a]

Tables 6 and 7 summarize the results of these analyses.

(a) Only on the 300° C oxide in an effort to obtain a better material balance. (The pyrolysis of the sample was carried out at about 875° C.)

Table 6

THERMAL HISTORY AND CHEMICAL AND X-RAY DIFFRACTION ANALYSES OF LABORATORY-PRODUCED OXIDES

| Preparation Temperature (° C) | Thermal Reduction Time (hours) | Total Uranium Found (gms U/gm) | Composition[1] (%) | | | Compounds Identified by X-Ray Diffraction | | |
|---|---|---|---|---|---|---|---|---|
| | | | $UO_3$ | $U_3O_8$ | $UO_2$ | Major | Intermediate | Minor |
| 300 | 6 & 12 | 0.8034 | 96 | - | - | Amorphous, No Pattern | | |
| 500 | 6 & 12 | 0.8419 | 34 | 66 | - | $U_3O_8$ | ND[2] | ND |
| 700 | 2 1/2 | 0.8420 | - | 98 | 2 | $U_3O_8$ | ND | ND |
| 900 | 2 1/2 | 0.8391 | - | 96 | 4 | $U_3O_8$ | ND | ND |
| 1100 | 2 | 0.8458 | - | 94 | 6 | $U_3O_8$ | ND | ND |
| 1300 | 2 | 0.8671 | - | 35 | 65 | $UO_{2.25}$ | ND | $U_3O_8$, $UO_2$ |

(1) Hypothetical from U(IV), U(VI), and total uranium analysis. Sample prepared at 300° C contained 0.85% $H_2O$.
(2) ND indicates that none was detected.

Table 7

SURFACE AREA, DENSITY, PARTICLE SIZE, AND CRYSTALLITE SIZE DETERMINATIONS OF LABORATORY-PRODUCED OXIDES

| Description[1] | Surface Area ($M^2$/gm) | Helium Density (gm/cc) | Average Particle Size (μ) | Average Crystallite Size[2] (μ) |
|---|---|---|---|---|
| 300 | 14.440 | 5.68 | 0.07 | - |
| 500 | 5.920 | 8.08 | 0.12 | 0.05 |
| 700 | 1.900 | 8.76 | 0.36 | 0.13 |
| 900 | 1.230 | 7.90 | 0.62 | 0.13 |
| 1100 | 0.536 | 8.19 | 1.37 | 0.13 |
| 1300 | 0.223 | 10.56 | 2.55 | 0.11 |

(1) Temperature (° C) at which sample was prepared.
(2) Sample prepared at 300° C was amorphous; Sample "1300" from $\beta UO_2$ measurement all others based on $U_3O_8$ measurements.

## Solubility Studies

Procedure - The solubility studies on the laboratory oxides were carried out in essentially the same way as on the process samples (a 50-milligram sample in 50 milliliters of synthetic lung fluid). However, there were some notable exceptions in the laboratory-oxide solubility studies:

1. Solubility studies were made in duplicate.

2. A modified sampling system was used that minimized the possibility of laminar flow (see Appendix A).

3. The soluble uranium samples in the fluorescence range (< 25 μgs U/ml, which on the laboratory oxide would be equivalent to a solubility of less than about 4%) were analyzed in quadruplicate.

4. Recycling solubility studies were made on a biweekly as well as weekly schedule.

5. Some modifications were made in the control program for this study, as indicated in Appendix B.

Results - Solubility results involving exposure of the laboratory-produced oxides to synthetic lung fluid for varying contact intervals are summarized in Table 8. Recycle contact experiments on a weekly and biweekly basis produced the results tabulated in Tables 9 and 10.

Table 8

SOLUBILITY OF LABORATORY-PRODUCED OXIDES AT VARIOUS CONTACT INTERVALS

| Description[1] | Total Uranium Dissolved (%) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 Week | | 2 Weeks | | 4 Weeks | | 8 Weeks | | 16 Weeks | |
| 300-A | 103 | (C)[2] | 103 | (C) | 89 | (C) | 111 | (C) | 133 | (C) |
| 300-B | 94 | (C) | 97 | (C) | 113 | (C) | 112 | (C) | 101 | (C)[3] |
| 500-A | 20.0 | (C) | 48.4 | (C) | 68.7 | (C) | 107 | (C) | 142 | (C) |
| 500-B | 24.0 | (C) | 35.5 | (C) | 80.2 | (C) | 45 | (C) | 98 | (C)[3] |
| 700-A | 0.92 | | 1.50 | | 2.11 | | 1.90 | | 2.31 | |
| 700-B | 1.27 | | 1.80 | | 1.82 | | 2.29 | | 2.73 | |
| 900-A | 0.58 | | 0.69 | | 1.07 | | 1.46 | | 3.17 | |
| 900-B | 0.60 | | 0.76 | | 0.96 | | 1.85 | | 1.88 | |
| 1100-A | 0.21 | | 0.26 | | 0.30 | | 0.30 | | 0.29 | |
| 1100-B | 0.18 | | 0.24 | | 0.26 | | 0.36 | | 0.46 | |
| 1100-C | 0.31 | | - | | - | | - | | - | |
| 1300-A | 0.12 | | 0.20 | | 0.13 | | 0.13 | | 0.14 | |
| 1300-B | 0.12 | | 0.13 | | 0.12 | | 0.12 | | 0.16 | |
| 1300-C | - | | 0.31 | | - | | - | | - | |

(1) Number indicates at what temperature (° C) sample was prepared.
(2) C indicates colorimetric analysis.
(3) Total sample analyzed.

## Discussion of the Results

According to Duval[9] there is some disagreement regarding the formula for uranium peroxide. The most commonly accepted formula is $UO_4 \cdot 2H_2O$, but recent investigators prefer the formula $UO_3 \cdot H_2O_2 \cdot H_2O$. The chemical compositions found for the oxides of known thermal histories are in good agreement with the reactions described by Duval:

$$UO_4 \cdot 2H_2O + \text{Free } H_2O \xrightarrow{< 90^\circ C} UO_4 \cdot 2H_2O + \text{Free } H_2O\uparrow,$$

$$UO_4 \cdot 2H_2O \xrightarrow{90 - 180^\circ C} UO_3 \cdot H_2O + H_2O_2\uparrow,$$

Table 9

SOLUBILITY OF LABORATORY-PRODUCED OXIDES AFTER ONE-WEEK RECYCLES

| Description[1] | Uranium Dissolved per Recharging (%) | | | | | | | | | | Total Uranium Dissolved[2] (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1st Cycle | 2nd Cycle | 3rd Cycle | 4th Cycle | 5th Cycle | 6th Cycle | 7th Cycle | 8th Cycle | 9th Cycle | 10th Cycle | |
| 300-1A | 103.2 (C)[3] | 6.5 (C) | 0.20 | 0.013 | 0.012 | < 0.001 | 0.001 | < 0.001 | < 0.001 | < 0.001 | 110 |
| 300-1B | 94.5 (C) | 12.4 (C) | 0.15 | 0.015 | < 0.001 | < 0.001 | < 0.001 | < 0.001 | < 0.001 | 0.001 | 107 |
| 500-1A | 20.0 (C) | 1.42 | 0.24 | 0.24 | 0.065 | 0.080 | 0.095 | 0.14 | 0.059 | 0.033 | 22.4 |
| 500-1B | 24.0 (C) | 4.4 (C) | 0.60 | 0.10 | 0.061 | 0.050 | 0.080 | 0.048 | 0.030 | 0.018 | 29.4 |
| 700-1A | 0.92 | 0.061 | 0.015 | 0.013 | 0.014 | 0.013 | 0.011 | 0.019 | 0.024 | 0.018 | 1.11 |
| 700-1B | 1.27 | 0.29 | 0.10 | 0.042 | 0.016 | 0.012 | 0.021 | 0.024 | 0.018 | 0.021 | 1.81 |
| 900-1A | 0.58 | 0.14 | 0.074 | 0.036 | 0.018 | 0.007 | 0.004 | 0.003 | 0.002 | < 0.001 | 0.86 |
| 900-1B | 0.60 | 0.15 | 0.073 | 0.042 | 0.030 | 0.016 | 0.013 | 0.006 | 0.007 | 0.006 | 0.94 |
| 1100-1A | 0.21 | 0.028 | 0.008 | 0.003 | 0.003 | < 0.001 | < 0.001 | < 0.001 | < 0.001 | < 0.001 | 0.25 |
| 1100-1B | 0.18 | | | | | Lost After First Cycle | | | | | |
| 1100-1C | 0.31 | 0.026 | 0.003 | < 0.001 | < 0.001 | 0.001 | 0.001 | < 0.001 | < 0.001 | < 0.001 | 0.34 |
| 1300-1A | 0.12 | < 0.001 | < 0.001 | < 0.001 | < 0.001 | < 0.001 | 0.001 | < 0.001 | < 0.001 | < 0.001 | 0.12 |
| 1300-1B | 0.12 | 0.003 | 0.002 | < 0.001 | < 0.001 | < 0.001 | 0.006 | < 0.001 | < 0.001 | < 0.001 | 0.13 |

(1) Number indicates the temperature (° C) at which the sample was prepared.
(2) No correction was made for a small positive bias resulting from the residual solution carried over from cycle to cycle.
(3) C indicates colorimetric analysis.

Table 10

SOLUBILITY OF LABORATORY-PRODUCED OXIDES AFTER TWO-WEEK RECYCLES

| Description[1] | Uranium Dissolved per Recharging (%) | | | | | Total Uranium Dissolved[2] (%) |
|---|---|---|---|---|---|---|
| | 1st Cycle | 2nd Cycle | 3rd Cycle | 4th Cycle | 5th Cycle | |
| 300-2A | 102.8 (C)[3] | 4.4 (C) | 0.38 | 0.29 | 0.45 | 108 |
| 300-2B | 96.9 (C) | 6.2 (C) | 0.68 | 0.16 | 0.039 | 104 |
| 500-2A | 48.4 (C) | 7.3 (C) | 1.0 | 7.0 (C) | 23.2 (C) | 87 |
| 500-2B | 35.5 (C) | 4.4 (C) | 4.8 (C) | 20.9 (C) | 21.8 (C) | 87 |
| 700-2A | 1.50 | 0.15 | 0.089 | 0.15 | 0.14 | 2.0 |
| 700-2B | 1.80 | 0.31 | 0.42 | 1.17 | 0.96 | 4.7 |
| 900-2A | 0.69 | 0.15 | 0.089 | 0.11 | 0.065 | 1.1 |
| 900-2B | 0.76 | 0.24 | 0.18 | 2.0 | 5.1 (C) | 8.3 |
| 1100-2A | 0.26 | 0.056 | 0.035 | 0.071 | 0.028 | 0.45 |
| 1100-2B | 0.24 | 0.055 | 0.047 | 0.030 | 0.014 | 0.39 |
| 1300-2A | 0.20 | Lost After First Cycle | | | | |
| 1300-2B | 0.13 | 0.011 | 0.003 | 0.003 | 0.001 | 0.15 |
| 1300-2C | 0.31 | 0.012 | 0.002 | 0.003 | < 0.001 | 0.33 |

(1) Number indicates the temperature (° C) at which the sample was prepared.
(2) No correction has been made for a small positive bias resulting from the residual solution carried over from cycle to cycle.
(3) C indicates colorimetric analysis.

$$UO_3 \cdot H_2O \xrightarrow{180 - 560^\circ C} UO_3 + H_2O\uparrow (UO_3 \text{ stable to } 672^\circ C), \text{ and}$$

$$6UO_3 \xrightarrow{672 - 800^\circ C} 2U_3O_8 + O_2\uparrow (U_3O_8 \text{ stable to } 946^\circ C).$$

All of these reactions were for an air atmosphere. In the present study in an argon atmosphere, chemical analyses and X-ray diffraction data were used to define the reaction products obtained. On this basis, the peroxide was reduced to the trioxide, then to the octoxide, and finally to the compound with the formula $UO_{2.25}$ ($\beta UO_2$) as the temperature was increased through the range studied (300 - 1300° C). Presumably, at some higher temperature, or probably over an extended time interval at the 1300° C level, the true dioxide would have been the final product.

To identify the compositions of the laboratory-prepared oxides, all were analyzed by standard X-ray diffraction powder pattern techniques and for uranium(IV), uranium(VI), and total uranium by chemical analysis. Calculated oxide compositions assumed the formation of the octoxide from mixtures of U(IV) and U(VI) with any excess forming the dioxide or trioxide, whichever was appropriate (see Table 6 and Figure 1). It was noted that apparently the X-ray diffraction method of compound identification completely failed to detect the trioxide present in the oxides prepared at 300 and 500° C, a condition which may have been attributable to the thermal-reduction technique used in the oxide preparation from the peroxide, which apparently formed a noncrystalline trioxide. This X-ray diffraction "blindness" may

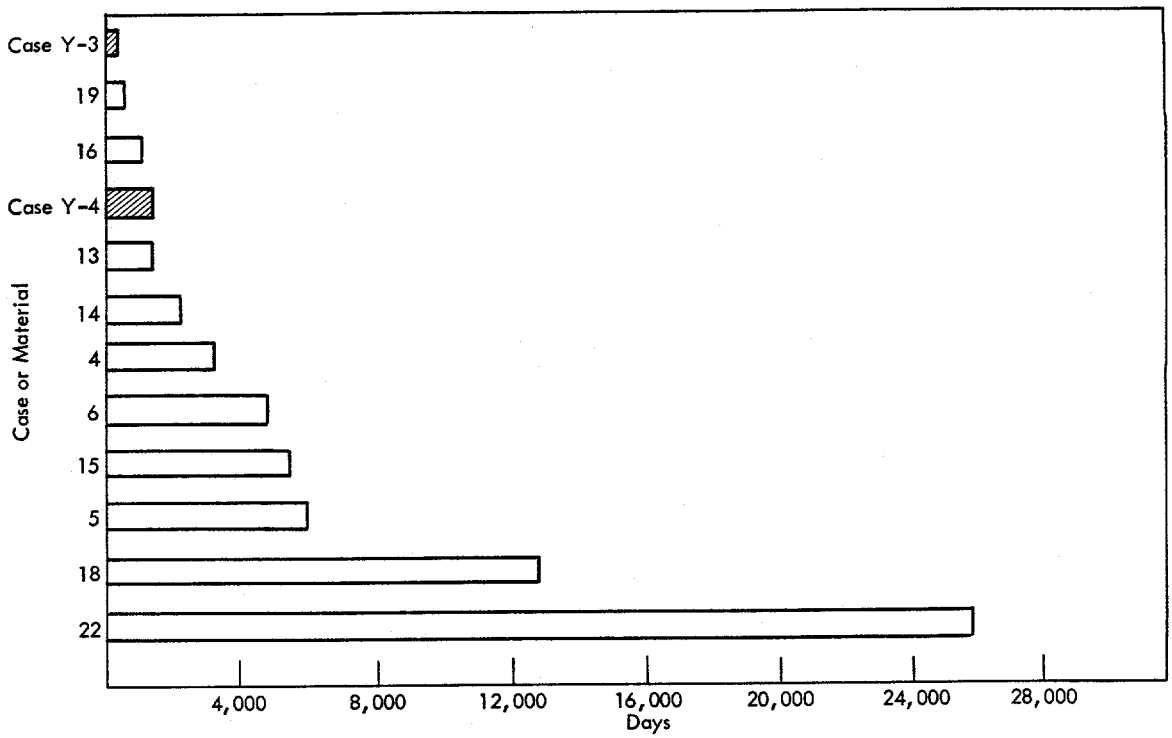


Figure 1. CHANGE IN PARTICLE SIZE AND COMPOSITION OF LABORATORY OXIDES WITH TEMPERATURE.

partially explain the wide variation in the solubility results obtained initially on the uranium process samples. It was not feasible to attempt similar valence-state uranium analysis on the process samples because of their high impurity level (Table 1).

Figure 1 also graphically illustrates the relationship between temperature and particle size. As expected, there appears to be a direct correlation between particle size and the temperature of the oxide preparation.

As was anticipated, the solubility of the laboratory-prepared oxides decreased as the temperature of the preparation increased (see Table 8 and Figure 2). No explanation can be given for the erratic solubility results sometimes exhibited by the oxide formed at 500° C. The high results were traced to evaporation losses encountered in spite of efforts to provide a sealed container. It was found that there was a volume loss of from 1.5 to 2% per week due to evaporation during the test period. Since total solubility was calculated from the analysis of an aliquant-corrected volume with no allowance for evaporation, the evaporation resulted in a positive bias to the result and likely accounts for the results being greater than 100%. The effect was verified for Samples 300B and 500B (both apparently dissolved completely) by total uranium content analyses of the sixteen-week sample. As shown in Table 8, a good material balance was obtained. (A comparable evaporation must

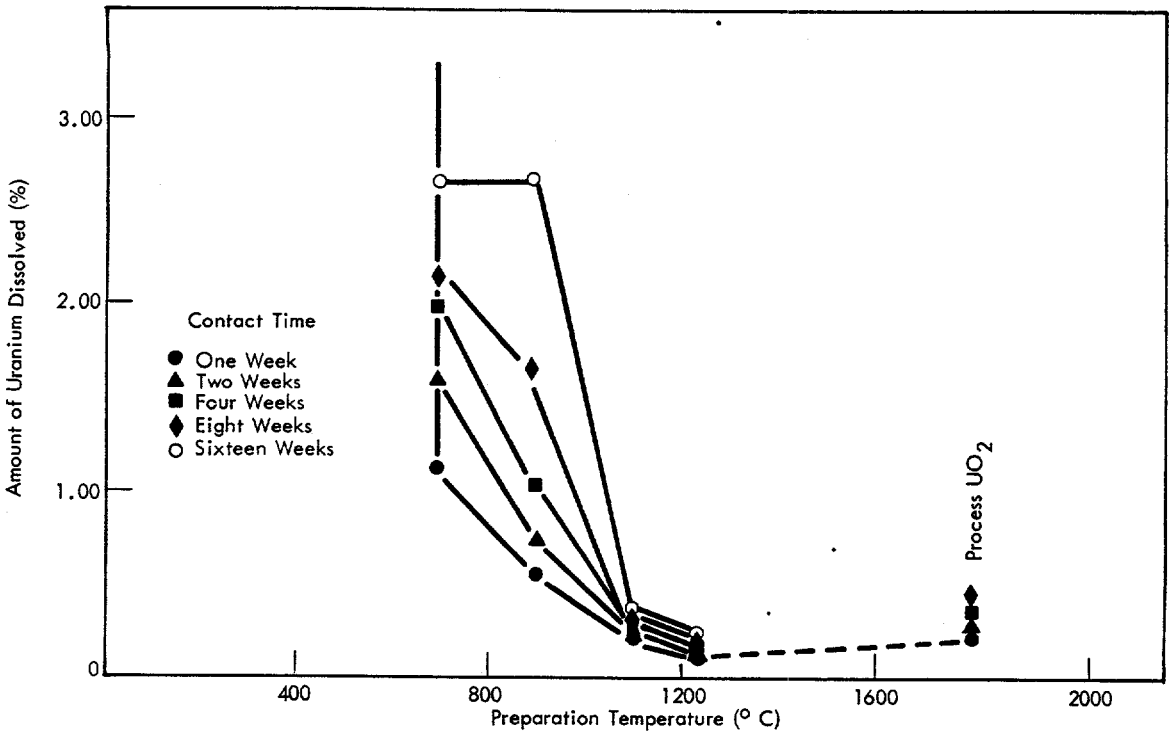


Figure 2. SOLUBILITY OF LABORATORY OXIDES AT VARIOUS CONTACT INTERVALS.

have also occurred during the process sample studies.) Except for the sixteen-week result for the series designated 900-A, the sample solubility results are all in their proper perspective.

The process sample of uranium dioxide (Specimen 21) that was studied in the initial phase of this characterization program has been included in Figures 1 and 2. This material, which was prepared at 1800° C for one hour, had a low solubility (~ 0.2%) and a relatively small average particle size (0.99 μ) that was obtained by grinding after ignition. The one, two, four, and eight-week solubilities from this sample (recalculated to two significant figures and found to be 0.32, 0.20, 0.18, and 0.25%, respectively) were statistically compared to the solubility data obtained on the 900, 1100, and 1300° C laboratory oxides (chosen because their particle sizes bracketed the particle size of the 1800° C $UO_2$) to determine if solubility might depend on the temperature of formation as well as particle size. No statistically significant difference in solubility with heats of formation independent of particle size could be demonstrated with the limited amount of data available. However, the fact that the solubility of the dioxide formed at 1800° C was not significantly different from that of the laboratory oxides formed at 1100 and 1300° C, which had larger particle sizes, suggests that the heat of formation decreases the solubility independently of the particle size.

Recycling solubility studies were made in duplicate for ten cycles with one week per cycle and five cycles with two weeks per cycle. The results of these recycling

studies are reported in Tables 9 and 10. More variability between the recycling studies in the total uranium dissolved for an oxide prepared at a given temperature will be readily noted. For example, the laboratory oxide prepared at 500° C had about 25% total uranium dissolved after ten cycles of one week per cycle, while the same oxide had about 87% total uranium dissolved after five cycles of two weeks per cycle. However, the results of the total uranium dissolved after biweekly cycles were in fair agreement with the 4, 8, and 16-week solubility data (Table 8). Anomalously, high solubilities were exhibited by one aliquot of each of the oxides formed at 700 and 900° C in the fourth and fifth cycle of the biweekly cycle study. All analytical results from the solubility studies have been included even though these exceptions have not been explained. The recycling solubility results are biased about 2 - 3% high because it was not practical to remove all of the solution between cycles. In spite of these anomalies, the recycle studies served adequately to demonstrate that the results obtained in the variable-interval study were not significantly influenced by saturation problems.

The collected measurements obtained from the laboratory-oxide samples have demonstrated that there was a decrease in the rate of dissolution of the uranium oxides as the temperature of preparation and/or particle size increased. Coincident increases in the particle size with increased preparation temperature made definite separation of these parameters impossible. The possibility of the presence of soluble uranium trioxide in oxides of relatively low thermal histories is offered as a possible explanation for the high initial solubility rates in such samples.

# CORRELATION OF TEST DATA WITH IN VIVO EXPERIENCE

## REVIEW OF DATA

Data from both the process and laboratory phases of the study were reviewed for in vivo significance. It is recognized that data obtained in vitro are difficult to interpret biologically because of the many factors which affect in vivo clearance and solubility which cannot be duplicated outside the body. However, this study gives information as to the relative in vivo solubility of the studied compounds and some general estimates on how these materials compare to the exposure materials of the five employees with long biological half lives.

## CLASSIFICATION OF MATERIALS STUDIED AS TO THEIR BIOLOGICAL SIGNIFICANCE

### Introduction

To look at the voluminous data in a simplified but meaningful manner, selected information was compiled from the process materials studied. These data are presented in Table 11. This information includes solubility data from process materials with information as to compounds and uranium content. (Similar information for the laboratory oxides is presented in Table 12.) As shown, the data fall into three categories: dilutes, solubles, and insolubles.

### Dilutes

Materials that had uranium concentrations below 0.5 percent were classified as dilutes. Y-12's experience with normal and depleted uranium and thorium, which have about the same or slightly higher alpha specific activities than do materials with these concentrations of enriched uranium, indicates that chances of significant exposures to materials of this specific activity are remote. The probability of these being the exposure material is thus exceptionally small.

### Solubles

All materials with uranium concentrations greater than 0.5 percent were classified as solubles if they showed a rate of dissolving which indicated that half the uranium would be in solution 380 days or less; ie, approximately 13% in 16 weeks. The reasons for selecting this degree of solubility as the dividing point between "solubles" and "insolubles" are: (1) 380 days was the shortest biological half life shown by the employees with the long chest half lives, and (2) in vivo biological half life on the respirable fraction of the tested materials would be shorter than in vitro half-dissolving times since the lung has methods of clearance other than dissolution and would

Table 11

SUMMARY OF DATA FROM PROCESS MATERIAL CHARACTERIZATION STUDIES

| Classification | Sample Number | Description | 16-Week Uranium Solubility (%) | Uranium in the Material (%) | Indicated Half-Dissolving Time(1) (days) |
|---|---|---|---|---|---|
| | | Dilutes | | | |
| | 9 | Caustic Fusion Residue(2) | 45.0 | 0.2 | - |
| | 12 | Salvage - I | 13.0 | 0.5 | - |
| | 3 | Reclaimed Sand(3) | 2.4 | 0.2 | - |
| | 11 | Firebrick | 1.6 | 0.5 | - |
| | | Solubles | | | |
| | 2 | $UO_3$ - Type A | 100.0 | 81.8 | < 112 |
| | 7 | $UO_3$ - Type B | 100.0 | 82.2 | < 112 |
| | 8 | $UF_4$ - Type A | 69.8 | 75.5 | < 112 |
| | 1 | $UF_4$ - Type B | 59.4 | 75.6 | 131 |
| | 20 | Salvage - II | 41.0 | 16.9 | 189 |
| | 10 | Column Leacher Residue | 22.0 | 1.6 | 353 |
| | | Insolubles | | | |
| $U_2O_7$(4) | 17 | Unleached Ash | 16.0 | 87.0 | 485 |
| $U_3O_8$(4) | 19 | Paper Ash - II | 12.0 | 15.8 | 647 |
| $U_3O_8$ | 16 | Paper Ash - I | 7.0 | 33.2 | 1,110 |
| $U_3O_8$ | 13 | High U Oxide - I | 5.1 | 83.1 | 1,520 |
| $U_3O_8$ | 14 | High U Oxide - II | 3.5 | 82.7 | 2,220 |
| $U_3O_8$ | 4 | High U Ash | 2.4 | 46.6 | 3,230 |
| $U_3O_8$ | 6 | Carbon Ash - II | 1.6 | 38.4 | 4,850 |
| $U_3O_8$ | 15 | Filter Bag Ash | 1.4 | 28.1 | 5,540 |
| $U_3O_8$ | 5 | Carbon Ash - I | 1.3 | 44.2 | 5,970 |
| $U_3O_8$ | 18 | Carbon Ash - III | 0.6 | 75.8 | 12,900 |
| $U_3O_8$ | 22 | Burned Uranium Chips | 0.3 | 84.6 | 25,900 |
| $UO_2$ | 21 | High-Fired $UO_2$ | 0.2 | 87.7 | - |

(1) Based on the percent solubility in 16 weeks and the assumption that percent solubility versus time is an exponential function.
(2) Results on dried sample. To convert to as-received material, multiply by 0.418.
(3) Sample appears inhomogeneous.
(4) Major uranium content as identified by X-ray diffraction.

contain a more favorable particle size for dissolving than did the test samples. Consequently, it was adjudged that materials which showed enough solubility to have a half-dissolving time of less than 380 days would be too soluble in vivo to be suspect materials.

## Insolubles

The insolubles consisted of materials with relatively high concentrations of uranium which were less soluble than those classified as being solubles. The relative insolubilities of these materials, expressed in terms of half-dissolving times, are tabulated

Table 12

SUMMARY OF DATA FROM LABORATORY OXIDE CHARACTERIZATION STUDIES

| Classification Insoluble[1] | Temperature of Formation of Oxide | 16-Week Solubility (%) | Uranium in the Material (%) | Indicated Half Dissolving Times[2] (days) |
|---|---|---|---|---|
| $UO_3$ (96%) | 300 | 100 | 80.3 | < 112 |
| $UO_3$ (34%) $U_3O_8$ (66%) | 500 | 100 | 84.2 | < 112 |
| $U_3O_8$ (98%) | 700 | 2.52 | 84.2 | 3,100 |
| $U_3O_8$ (96%) | 900 | 2.52 | 83.9 | 3,100 |
| $U_3O_8$ (94%) | 1100 | 0.38 | 84.6 | 20,400 |
| $U_3O_8$ (35%) $UO_2$ (65%) | 1300 | 0.15 | 86.7 | 51,000 |

(1) Based on Uranium(IV), Uranium(VI), and total uranium analyses.
(2) Based on the percent solubility in 16 weeks and the assumption that the percent solubility versus time is an exponential function.

and compared in Figure 3 with the shortest and longest biological half lives of the Y-12 cases. By comparison, it appears that many of the oxides listed are insoluble enough to be potentially the exposure materials of these persons.

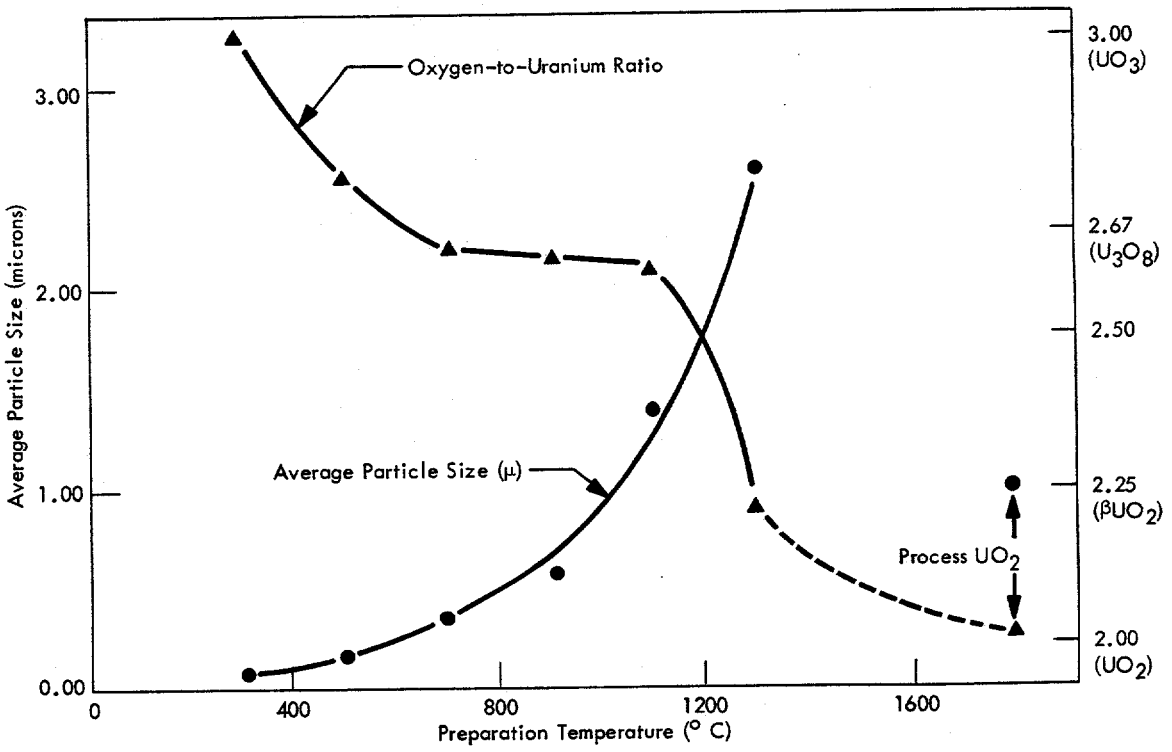


Figure 3. COMPARISON OF HALF-DISSOLVING TIMES AND CHEST HALF LIVES.

## SELECTION OF THE MOST LIKELY EXPOSURE MATERIAL

### Elimination of Insolubles Due to Unavailability

The most likely exposure materials would be expected to come from the insolubles. Table 11 indicates that burned uranium chips and high-fired $UO_2$ are the most insoluble of these materials. However, these two cannot be considered as likely exposure materials due to the fact that none of the persons have been exposed to burned uranium chips since it was specially prepared for comparison purposes only, and only one of the persons worked in the area where high-fired $UO_2$ was prepared.

### Particle Size Effect on Solubility

To better understand and/or establish the reason for the wide variance in solubility among the octoxide compounds, they were compared as to particle size. As shown in Table 5, the amount of these materials which would go through a 100-mesh (150-μ) screen varies from 29 to 90%. However, it was expected that the screenable portion of these samples would account for almost all of their solubility because of the high surface area-to-volume ratio of this portion compared to the nonscreenable portions. (The ratio of surface to volume is 150 times as high for a 1-μ particle as for a 150-μ particle.) A plot of solubility as a function of the screenable portion particle size is presented in Figure 4. The fact that these data show a correlation coefficient of 0.58, which is significantly different from zero, supports the supposition that most of the solubility came from the screenable portion and suggests that solubility is a function of the particle size.

### Selection of Three Ashes as the Most Likely Exposure Material

It was noted that five materials classified as ashes had relatively high particle sizes and were the most insoluble of the remaining suspect materials. In view of their similarity in origin, solubility, and particle size, it appears that the most likely exposure material(s) come from this group.

To further evaluate the relative probability of these five ashes being the exposure material(s), two actions were taken: (1) the average solubilities for the 4th, 8th, and 16th week of the sixteen-week solubility study and the ten-week recycling solubility study were compiled for comparison (in Table 14) to reduce the possibility of deviant results; and (2) the average percent solubility was adjusted for each material by dividing by the screenable fraction. This adjustment provides an estimate of the degree of solubility that would have been experienced if the tests had been run on the screenable portion only. The solubility of this portion is the more significant one from an in vivo standpoint since the nonscreenable portion was well above the respirable size. From a study of Table 13, three ashes: carbon-III, filter bag, and high U, were found to be the most insoluble process materials tested.

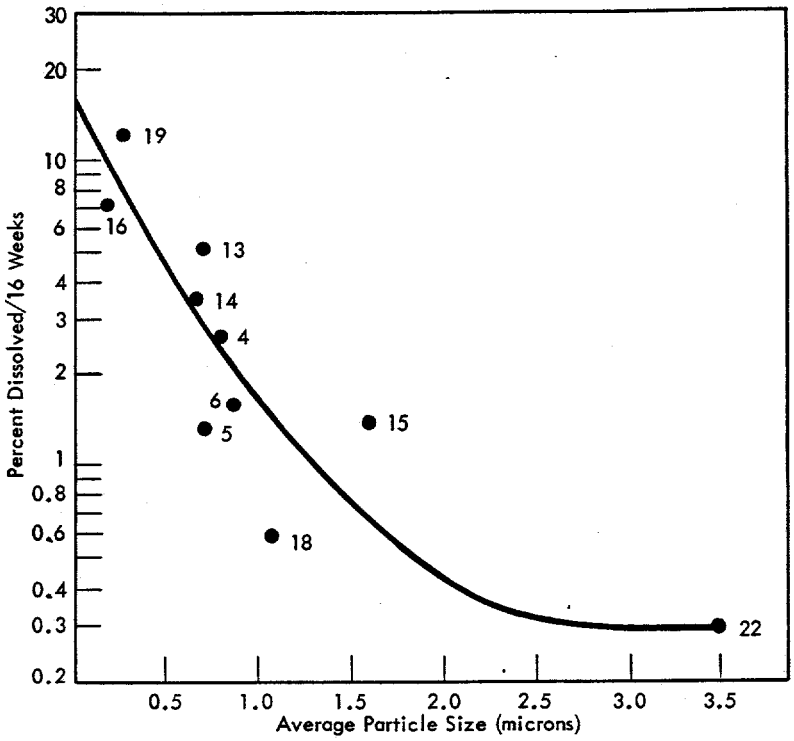


**Figure 4. PERCENT OF PROCESS SAMPLES DISSOLVED AS A FUNCTION OF THEIR PARTICLE SIZE. (Numbers Next to the Data Points are Sample Numbers; See Table 11)**

Table 13

DATA FROM THE FIVE MOST INSOLUBLE PROCESS ASHES

| Sample Number | Description | Solubilities (percent dissolved) Weeks 4 | 8 | 16 | 10 | Average | Percent Screenable | Adjusted Solubility Average (percent dissolved) | Average Particle Size (μ) |
|---|---|---|---|---|---|---|---|---|---|
| 18 | Carbon Ash - III | 0.2 | 0.4 | 0.6 | 0.3 | 0.4 | 0.82 | 0.5 | 1.1 |
| 15 | Filter Bag Ash | 0.8 | 1.0 | 1.4 | 0.8 | 1.0 | 0.90 | 1.1 | 1.6 |
| 4 | High U Ash | 0.6 | 0.6 | 2.4 | 0.9 | 1.1 | 0.90 | 1.2 | 0.86 |
| 6 | Carbon Ash - II | 0.7 | 2.0 | 1.6 | 0.8 | 1.3 | 0.46 | 2.8 | 0.89 |
| 5 | Carbon Ash - I | 0.9 | 1.2 | 1.3 | 0.9 | 1.2 | 0.29 | 3.8 | 0.73 |

Besides being ashes, three other common parameters were found to be present. These characteristics are discussed in the paragraphs that follow.

High-Temperature Thermal Histories - The ashes all come from salvage from areas where the uranium is subjected to high temperatures. The uranium in the carbon-III was originally uranium dicarbide and had been heated to temperatures near 2300° C. Both the filter bag and the high U ash came from the enriched uranium foundry.

These salvage materials arose from casting operations in which the temperatures were approximately 1300° C. In addition, all of these materials were reduced to ash with the use of oxygen. The temperatures from such a burning are not accurately known but are logically expected to be relatively high.

Large Particle Size - All three have relatively high average particle sizes. As shown in Table 5, the carbon-III and filter bag ashes showed the largest particle sizes of the materials under consideration, and the high U ash showed the fourth largest particle size.

Impurity Level - Identifiable impurities above 5% were found in all of these ashes (Table 1).

On the basis of this information, these three materials are adjudged to be the most likely exposure materials.

## ANIMAL EXPERIMENTS

Selection of the ashes containing the octoxide as the most likely exposure materials raises a question as to why the Y-12 cases show so much longer biological half lives in the chest than is considered normal. The nominal value of 120 days for the lung half life, accepted by the International Council on Radiation Protection,[3] has been confirmed for uranium by animal studies which were performed using either the octoxide or the dioxide (which the laboratory studies described here indicate is as insoluble as the octoxide). Such animal studies[10 - 13] have consistently shown shorter biological half lives than those exhibited by the cases in question, which is illustrated by the information contained in Table 14. However, the studies were brief, only a small number of animals were used, and the experimenters were not very confident of the results.

Table 14

SUMMARY OF INFORMATION FROM FOUR ANIMAL STUDIES

| Reference | Oxide Used | Animal | Number of Animals | Length of Exposure | Biological Half Life Quoted | Average Particle Size[2] (μ) | Author Evaluation |
|---|---|---|---|---|---|---|---|
| Voegtlin[10] | $UO_2$ | Dogs | "Few" | 2 years | 48 - 147 days | 0.33 - 0.42 | Critical insufficiency of data available. |
| | $UO_2$ | Rats | (1) | 2 years | ~120 days | | |
| Hodges[11] | $UO_2$ | Rat | (1) | (1) | 150 - 180 days | (1) | Limited data. |
| Fish[12] | $U_3O_8$ | Dogs | 9 | 4 months | 120 days | ~0.40[16] | Preliminary findings. |
| Marrow[13] | $UO_2$ | Dog | 3 | 80 days | 180 - 200 days | 0.37 - 0.42 | |

(1) Unknown.
(2) The information on particle size presented by the authors was converted to average particle size for comparison with the Y-12 data by using conversion factors suggested by Raabe.[15]

The most likely reason for this shorter half life in the animal experiments appears to be a difference in the exposure materials. Although information on these exposure materials is not complete, it appears that the oxides used were different in the following characteristics:

1. The dioxide used in most of the studies came from the reduction of the trioxide with hydrogen, a reaction that takes place readily at ~600° C.[14] Such temperatures are less than those experienced in the thermal histories of the three most insoluble ashes in the Y-12 study.

2. Available particle size information from the animal studies converted to average particle size for ready comparison with the particle size data from this study is given in Table 14. All animal experimental oxides indicate a smaller average particle size than was found on the screenable portion of the most likely process exposure materials.

3. The chosen ashes showed identified impurity levels of from 5 to 30%. Voegtlin[10] says the oxide used in his animal studies was greater than 99.5% pure. Although no specific information is available from the reports of the other studies, it seems safe to assume that these experiments were also conducted with compounds that were relatively pure when compared to the process ashes.

# CONCLUSIONS

The following conclusions can be stated:

1. Certain of the process materials checked were too soluble and/or dilute to be considered as likely exposure materials.

2. In almost all likely exposure materials, uranium octoxide was present. The large variation in the observed solubility for this group may have been influenced by the presence of small amounts of the trioxide or other factors associated with formation temperature, as well as particle size.

3. The solubility studies of laboratory oxides indicated that only two variables could be related to relative solubility: chemical composition and particle size. Both of these parameters were related to the thermal history of the oxide.

4. The selection of uranium octoxide as the most likely exposure material for persons showing a 380 - 1470-day biological half life is not supported by animal experimental data with insoluble oxides. Such data suggest a lung or chest half life of about 120 days.

5. There are differences in particle size, thermal histories, and contamination content between the animal studies and the Y-12 process materials, which could explain the difference in the in vivo solubility.

It is recommended that an animal study be made with the respirable fraction of the three octoxide-containing combustion process ashes ascertained to be the most likely exposure materials. If such a study shows a long biological half life in the animals, further investigations should be conducted as necessary to ascertain the reason for the high in vivo insolubility of such compounds.

Such a study would add to the information available on the biological clearance rate for insoluble uraniums. Currently, there is a paucity of such information.

## ACKNOWLEDGEMENTS

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# APPENDIX A

# SOLUBILITY SAMPLING APPARATUS

## INTRODUCTION

A suction-type sample filtering system was devised for use with the process-material solubility studies. Experience indicated that certain modifications would be desirable. These modifications led to a pressurized filtering apparatus, used for the laboratory oxide filtrations. Both systems and their use are described separately.

## PROCESS MATERIAL

### Apparatus

The sampling apparatus used for the process-samples solubility studies is illustrated in Figure A-1. The glass immersion tube had a medium-porosity, 10-millimeter-diameter glass frit which acted as a support for the 15-millimeter-diameter, 0.45-micron membrane filter for the suction filtration.

### Sampling Technique

The filtrate was drawn above the calibration mark on the 20-milliliter pipette and the filled pipette removed from the system. The solution was then drained to the calibration mark and the sample transferred to a 25-milliliter volumetric flask. The pipette was rinsed with about 2.5 milliliters of 2-molar nitric acid which was added to the contents of the flask. The acid rinse served to remove any adsorbed uranium from the pipette and to acidify the sample. The glass sampling apparatus was thoroughly cleaned with additional acid and distilled water in order to minimize the possibility of cross contamination.

In the recycling solubility studies, the membrane filter was left in the vial after taking the sample to dryness.

## LABORATORY OXIDES

### Modified Sampling Apparatus

A redesigned sampling apparatus was used for the solubility studies of the oxides of known thermal histories. The apparatus was designed around a hypodermic syringe membrane filter holder made for dispensing filtered solutions. Pressure was used to effect the filtration. An illustration of this pressurized filtering apparatus is presented in Figure A-2. The laminar flow problem was minimized using this plastic holder since the 13-millimeter-diameter membrane filter was held in place by screwing the

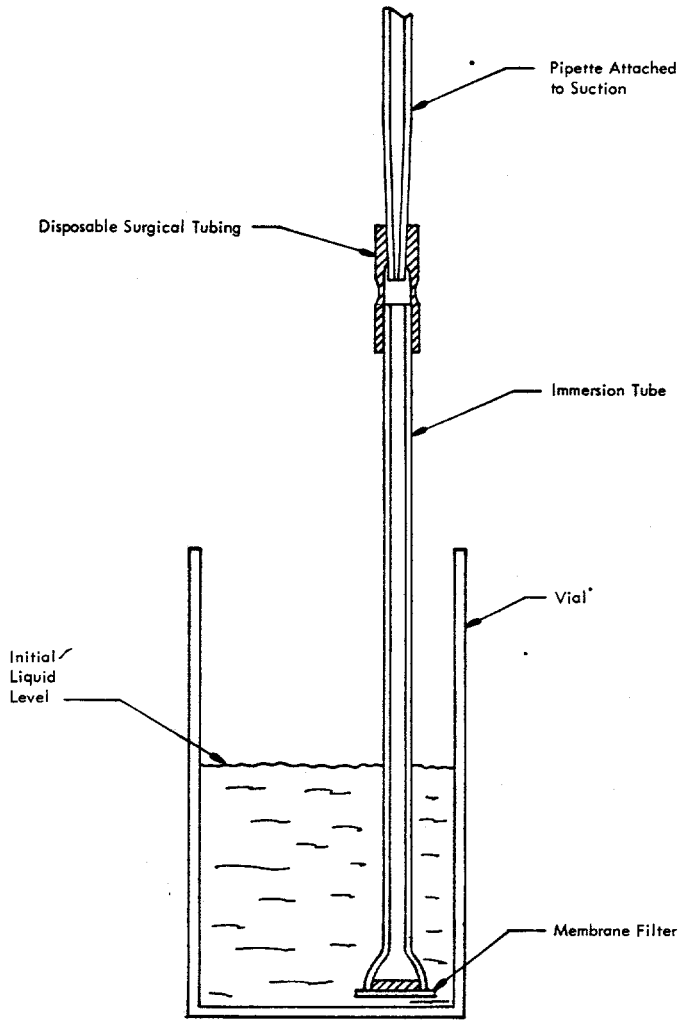


**Figure A-1. SAMPLING APPARATUS FOR PROCESS SAMPLES.**

two parts of the holder together, thus creating a 2-millimeter-wide circumferential seal.

## Components of the Filtering Apparatus

The parts comprising the filtering apparatus are described in the sections that follow.

Pipette - Volumetric; 20 milliliters.

Tubing - Surgical; 1/8-inch ID, 3/64-inch wall, ~ 3/4-inch long.

Filter Holder - Polypropylene, Millipore Swinnex-13.

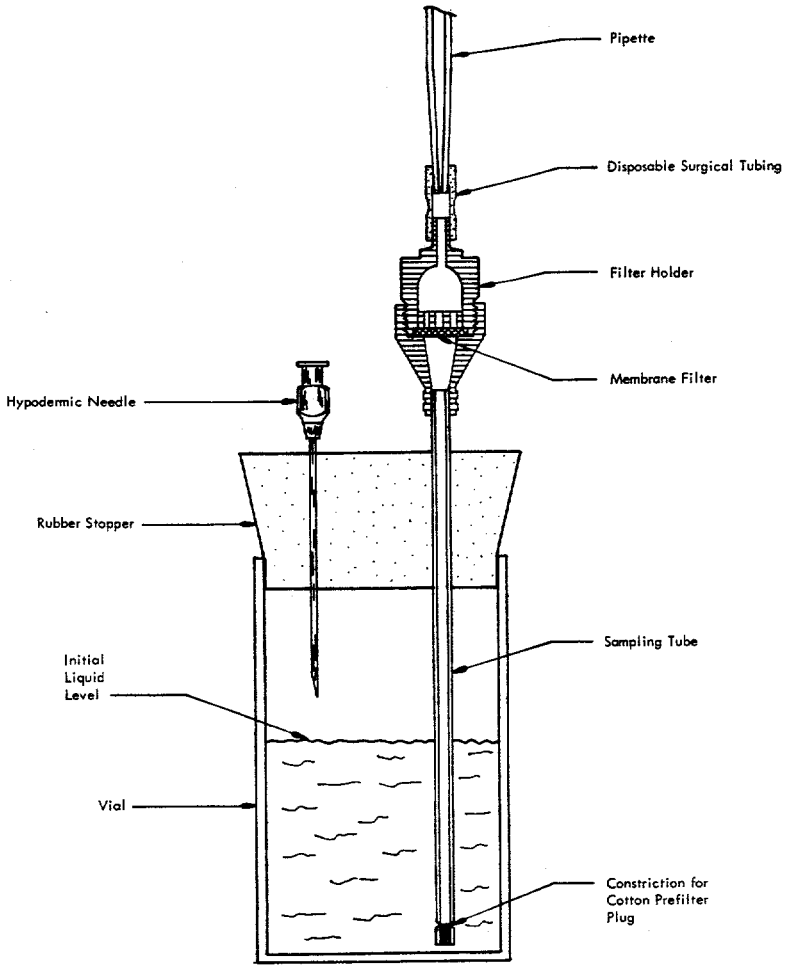


**Figure A-2. PRESSURIZED SAMPLING APPARATUS FOR LABORATORY OXIDES.**

Membrane Filter - Millipore HA (0.45-μ pore); 13 millimeters in diameter.

Rubber Stopper - Number 10 solid, drilled with 15/64 and 7/64-inch bits.

Glass Sampling Tube - Constricted slightly about 6 millimeters from one end to support the cotton "prefilter"; ~ 3.4 millimeters in OD and ~ 110 millimeters long. (The tube was selected to fit snugly inside the threaded inlet of the filter holder.)

Hypodermic Needle - Stainless steel; 16 gauge, 2 inches long.

Surgical Cotton - Used as a prefilter plug.

Vial - Polystyrene with a screw cap; 1 3/4 inches in diameter and 3 inches high.

Rubber Bulb - Double action, with a Leur-lock fitting from a syringe attached to the exhaust valve of the bulb by a short length of rubber tubing; 2 - 3-ounce capacity.

Pressure Inlet Adapter - L shaped with a Leur-lock fitting from a syringe soldered to one leg of copper tubing; 6 inches in length and made of 3/8-inch OD copper tubing.

Clamping Jig - Fabricated from clear plastic sheets and cemented together creating a work area of about 5 5/8 by 6 inches; 3/8 by 6 by 7-inch base with a 1 3/8-inch-thick, 2 9/16-inch-high, and 6-inch-long back. (A toggle clamp, "Knu-Vise" VC-200, was mounted on the upper surface of the back to afford clamping action.)

Argon Gas - Cylinder equipped with a two-stage reducing valve.

Rubber Pressure Tubing - Used to connect the reducing valve to the pressure inlet adapter; 5/8-inch OD, 1/4-inch ID. (Hose clamps were used on these connections.)

Apparatus Support Stand - Supplied with a burette clamp to hold the pipette.

Initially it had been planned to use the membrane filter and filter holder with suction to effect filtration. However, when an air bubble would get into the filter holder during the filtration, the filtering action would cease. This condition was found to be attributable to a vapor lock since a pressure of 32 psi is required to force an air bubble through a water-wet Millipore HA filter.[17] This vapor-lock filtration problem was eliminated upon going to the pressurized filtration apparatus providing the filter holder was free of moisture prior to using.

Experiments were conducted to determine the practicality of using the pressurized filtering apparatus from a safety standpoint. When a water-wet membrane filter was in the holder in the apparatus, it was found that a pressure of approximately 25 psig was required to effect the separation of an apparatus component from the system. At this point, a "safety valve" was created by the partial separation of the rubber stopper from the polystyrene vial. Unexpectedly, the vial did not rupture.

## Sampling Technique

The apparatus was assembled as illustrated in Figure A-2 with the stopper clamped to the vial in the clamping jig. The clamp "arm" was positioned across the diameter of the stopper between the sampling tube and the needle. By using the double-action rubber bulb attached to the hypodermic needle, the pressure on the vial could be carefully controlled to force the solution up through the cotton "prefilter" in the sampling tube, through the dry membrane filter, and into the lower stem of the pipette. The bulb was then removed from the needle, the pressure inlet tube attached to the needle, and argon pressure (about 8 psig) applied to the system to

effect the filtration until the filtered solution level had risen above the calibration mark of the pipette. After shutting off the argon pressure, the filtered sample in the pipette was removed from the system, the solution drained to the calibration mark of the pipette, and the sample transferred to a 25-milliliter volumetric flask. The pipette was rinsed with about 2.5 milliliters of 2-molar nitric acid which was added to the contents of the volumetric flask.

In the recycling solubility studies, the cotton prefilter plug used in the sampling tube was removed from the tube and left in the vial prior to the addition of 50 milliliters of new synthetic lung fluid for another cycle.

Cleaning and Reuse of the Apparatus

The surgical tube connection between the filter holder and pipette was discarded. The pipette was thoroughly cleaned with acid and water between samples in order to minimize cross contamination. Likewise, after removing the cotton prefilter, the glass sampling tube below the rubber stopper was immersed in acid and flushed thoroughly with water to clean it. Cleaning the filter holders was done in a batch process. Each filter holder was unscrewed and the membrane filter and solution inside the holder were salvaged. Both parts of the filter holder were flushed with a jet of distilled water. The excess water was shaken out of the filter halves and the disassembled filter holders were then immersed for one hour in about 2-molar nitric acid. After leaching, the acid solution was decanted from the mixture and the holders washed 5 or 6 times with distilled water. The part of the holder having the filter support was again flushed with a jet of distilled water, the excess water shaken out, and a jet of air passed through the part to remove any droplets of water inside. The unassembled filter holders were then allowed to dry overnight at room temperature before loading with a new membrane filter.

An exceedingly useful vacuum tweezer unit[a] was used to minimize damage to the delicate (150-μ thick) membrane filter during the loading of the holder. The vacuum tweezer unit was equipped with a 20-gauge pickup tip having a 1/4-inch-diameter polyvinyl suction cup.

(a) Model V-100; Ultrasonic Industries, Inc, Rahway, New Jersey.

# APPENDIX B

# CONTROL PROGRAMS

## INTRODUCTION

Control programs were established to provide confidence and validity for the fluorescent measurement of small amounts of uranium in solution. Since the program was modified somewhat between the process material and laboratory oxide studies, each will be discussed separately. To further substantiate the validity of the results, a container adsorption study was also conducted.

## PROCESS MATERIAL STUDY

Control programs were maintained to further assure the reliability of fluorometric results. Two controls containing 0.20 μg U/ml and two controls containing 2.00 μgs U/ml were submitted with each group of process samples submitted for direct fluorometric analysis. These controls were prepared in synthetic lung fluid and, like the process samples, were acidified with nitric acid. Altogether 27 of each of the controls were submitted for analysis over about a sixteen-week interval and the results statistically evaluated. The limit of error (0.95) for a single determination was found to be ± 20% and ± 12% relative for the 0.20 and 2.00 μgs U/ml controls, respectively. As related to sample solubility results, these values would be equivalent to 12.5 and 125 μgs total uranium dissolved.

Because of the high and variable impurity level of the process specimens, a spiking program[18] was also maintained throughout this study in conjunction with the prepared control program. Based on the results obtained, none of the process materials studied contained impurities capable of significantly quenching the uranium fluorescence.

## LABORATORY OXIDE STUDY

Two controls containing 0.05 μg U/ml and two controls containing 0.20 μg U/ml were submitted with each group of samples submitted for fluorometric analysis. These controls had been prepared in synthetic lung fluid and, like the samples, were acidified with nitric acid. These 0.05 and 0.20 μg U/ml controls would correspond to about 0.007 and 0.030% dissolved uranium on the laboratory oxides. Altogether, 36 of each of the controls were submitted for analysis over about a sixteen-week interval and these results statistically evaluated. The limit of error (0.95) for a single determination was found to be ± 30% and ± 14% relative for the 0.05 and 0.20 μg U/ml controls, respectively.

## CONTAINER ADSORPTION STUDY

A study was made to determine if the adsorption of uranium on the surface of the polystyrene sample container significantly affected the result of the solubility studies. The results of this study, as summarized in Table B-1, indicate that adsorption on the container walls was not significant at uranium concentrations of 12.5 µgs/50 mls or greater. These adsorption results have not been corrected for

Table B-1

ADSORPTION STUDIES

| Sample Description[1] | Time in the Incubator | Uranium Added (µgs) | Uranium Found (%) | | |
|---|---|---|---|---|---|
| | | | Solution | Leachings | Total |
| AS-A | 1/2 hr | 125 | 102 | - | 102 |
| AS-B | 1/2 hr | 12.5 | 97 | - | 97 |
| AS-C | 1/2 hr | 1.25 | 92 | - | 92 |
| AS-A1 | 1 wk | 125 | 98 | 5 | 103 |
| AS-B 1 | 1 wk | 12.5 | 107 | 4 | 111 |
| AS-C1 | 1 wk | 1.25 | 62 | 4 | 66 |
| AS-A2 | 2 wks | 125 | 81 | 15 | 96 |
| AS-B2 | 2 wks | 12.5 | 86 | 16 | 102 |
| AS-C2 | 2 wks | 1.25 | 82 | 8 | 90 |
| AS-A3 | 4 wks | 125 | 90 | 15 | 105 |
| AS-B3 | 4 wks | 12.5 | 107 | 8 | 115 |
| AS-C3 | 4 wks | 1.25 | 64 | 8 | 72 |
| AS-A4 | 8 wks | 125 | 104 | 7 | 111 |
| AS-B4 | 8 wks | 12.5 | 98 | 18 | 116 |
| AS-C4 | 8 wks | 1.25 | 56 | 13 | 69 |

(1) One milliliter of uranyl nitrate solution was added to 50 milliliters of snythetic lung fluid in a polystyrene vial (100 mls capacity) and shaken in an incubator at body temperature for varying time intervals.

evaporation, but since all sample results of importance to the conclusions were found to be above this concentration level, it was concluded that container adsorption did not affect the study significantly.

# APPENDIX C

# PREPARATION OF THE LABORATORY OXIDES

## INTRODUCTION

A batch of enriched uranium metal turnings was obtained as the starting material for the preparation of oxides with known thermal histories. This metal had a nominal purity level of 99.9+% uranium.

## PROCEDURE

### Preparation of Uranium Peroxide

Approximately 50 grams of the uranium metal turnings were dissolved in a slight excess of nitric acid with heating. The solution was evaporated to dryness to remove excess nitric acid. The uranyl nitrate cake was dissolved in about 1500 milliliters of water and adjusted to a pH of 2.0 by the addition of nitric acid. The uranium was precipitated at room temperature by the addition of hydrogen peroxide (30%) with stirring. The pH of the solution was maintained at 2.0 by the addition of ammonia solution. An excess of hydrogen peroxide was added to insure completeness of the precipitation. After digesting about one hour at room temperature, the precipitate was filtered off, washed 4 or 5 times with hot distilled water, and dried overnight at 90° C. A second batch (50 gms U) was prepared and the two batches combined, ground, and used as starting material for the preparation of the oxide samples of known thermal histories. Gravimetric uranium analyses indicated that the dried and ground precipitate was 98.5% uranium peroxide.

### Thermal Reduction

A tube furnace was used for the thermal reduction of the uranium peroxide. An argon sweep gas was maintained in the combustion tube at all times during the complete heating, reduction, and cooling cycles. A thermocouple was placed inside the combustion tube adjacent to the combustion boat to facilitate temperature monitoring. Because of apparatus size limitations, the oxides were generally prepared in two batches (10 gms $UO_4$/batch). Thermal reduction conversion factors (oxide to peroxide) were obtained on all reductions to monitor the product control. Extended reduction times of 6 and 12 hours for the 300 and 500° C specimens produced equivalent weight losses. The shorter reduction times for the higher fired specimens were in line with standard laboratory practice. A tendency to sinter was noted for the 1300° C specimen. (The other specimens sintered to a lesser extent.)

After thermal reduction, the oxides were ground and sieved through a 100-mesh sieve (150 μ). Preparations through 900° C were reheated in an argon atmosphere to constant weight to eliminate any moisture picked up during grinding and sieving.

## REFERENCES


(1) McRee, P. C., West, C. M., and McLendon, J. D., Editors; Y-12 Radiation Safety Manual, Physics and Industrial Hygiene Program, Y-1401; Union Carbide Corporation-Nuclear Division, Y-12 Plant, Oak Ridge, Tennessee; May 11, 1965.

(2) West, C. M. and Scott, L. M.; An Evaluation of Cases Showing Uranium Chest Burdens with Long Biological Half Lives, Y-KB-56, Union Carbide Corporation-Nuclear Division, Y-12 Plant, Oak Ridge, Tennessee; December 7, 1965.

(3) "Report of ICRP Committee II on Permissible Dose for Internal Radiation", Health Physics, 3 (1960).

(4) Klug, H. P. and Alexander, L. E.; X-Ray Diffraction Procedures; John Wiley and Sons, Inc, New York, New York (1954).

(5) Azaroff, L. V. and Buerger, M. J.; The Powder Method in X-Ray Crystallography; McGraw-Hill Book Company, New York, New York (1958).

(6) Gamble, G. L.; Chemical Anatomy, Physiology, and Pathology of Extracellular Fluid, A Lecture Syllabus; Harvard University Press, Cambridge, Massachusetts (1952).

(7) Emmett, P. H.; "The Measurement of the Surface Areas of Finely Divided or Porous Solids by Low Temperature Adsorption Isotherms", Advances in Colloid Science, p 1; Interscience, New York, New York (1942).

(8) Schumb, W. C. and Rittner, E. S.; "A Helium Densitometer for Use with Powdered Materials", J Am Chem Soc, 65, p 1692 (1943).

(9) Duval, C.; Inorganic Thermogravimetric Analysis, p 662; Elsevier Publishing Company, New York, New York (1963).

(10) Voegtlin, C. and Hodge, H. C.; The Pharmacology and Toxicology of Uranium Compounds, National Nuclear Energy Series, Division VI, Vol I, Parts III and IV; McGraw-Hill Book Company, Inc, New York, New York (1953).

(11) Hodge, H. C. and Thomas, R. G.; "Health Hazards from the Inhalation of Insoluble Uranium and Thorium Oxides", Proceedings of the Second United Nations International Conference on Peaceful Uses of Atomic Energy, 23, p 739 (1958).

(12) Fish, Birney R.; "Inhalation of Uranium Aerosol by Mouse, Rat, Dog, and Man", Inhaled Particles and Vapors; Pergamon Press, London (1961).

(13) Marrow, P. E., Gibb, F. R., and Johnson, L.; "Clearance of Insoluble Dust from the Lower Respiratory Tract", Health Physics, 10, p 543 (1964).

(14) Patton, F. S., Googin, J. M., and Griffith, W. L.; Enriched Uranium Processing; The MacMillian Company, New York, New York (1963).

(15) Task Group on Lung Dynamics; "Disposition and Retention Model for Internal Dosimetry of the Human Respiratory Tract", Health Physics, 12, p 173 (1966).

(16) Fish, Birney R.; Personal Communication.

(17) "Microchemical and Instrument Analysis", Application Data Manual ADM-70; Millipore Filter Corporation, Bedford, Massachusetts (1963).

(18) Price, G. R., et al; "Fluorophotometric Determinations of Uranium", Anal Chem, 25, p 322 (1953).